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(54) Title: AMPHOTERIC DERIVATIVES OF ALIPHATIC POLYAMINES WITH FATTY ACIDS, ESTERS OR TRIGLYCERIDES		
(57) Abstract <p>Amphoteric derivatives of aliphatic polyamines, such as diethylenetriamine or triethylenetetramine reacted with long chain fatty acids, esters or triglycerides from various natural or synthetic sources are effective in the softening/texture modification of substrates such as paper, textiles, human skin surfaces and hair tresses, as well as in applications for metal working and lubrication. The polyamines are first reacted with fatty acids, esters or triglycerides derived from various animal, vegetable or synthetic sources ranging in molecular distribution from butyric through erucic acids (e.g. milkfat, soy bean oil, rapeseed oil) to form diamides or imidazolines; they are then further reacted with unsaturated or halogenated carboxylic acids, carboxylated epoxy compounds or acid anhydrides (e.g. acrylic acid, itaconic acid, chloroacetic acid, maleic anhydrides octadecenyl anhydride) to form the various amphoteric structures.</p>		

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AMPHOTERIC DERIVATIVES OF ALIPHATIC POLYAMINES WITH FATTY ACIDS, ESTERS OR TRIGLYCERIDES

FIELD OF THE INVENTION

The present invention relates to amphoteric surface active agents, and more particularly to amphoteric derivatives of aliphatic polyamines, such as diethylenetriamine reacted with long chain fatty acids, esters or triglycerides. In addition to being novel materials, the amphoteric derivatives of this invention are useful in a variety of applications including the softening/texture modification of substrates such as paper, textiles, human skin surfaces and hair tresses, as well as in applications for metal working, and lubrication.

BACKGROUND OF THE INVENTION

Amphoteric compositions of various types including derivatives of polyamines are known and have been used over the years for a variety of applications including surfactants in detergent and dishwashing formulations, fabric and paper treating compositions, metal treating and corrosion inhibition, and the like. For example, U.S. Patent No. 2,999,069 to Masci teaches detergent compositions containing amphoteric derivatives of amidoamines but does not teach or disclose diamide or polyamide compositions having a reactive secondary, internal nitrogen amine site which is carboxyalkylated as provided in the present invention. Liquid dishwashing compositions disclosed in European Patent Application No. 92 203 230.5 to Jadwiga Palicka include amphoteric surface active agents; however, neither diamide nor polyamide compositions having a secondary, internal nitrogen amine site which is carboxyalkylated are disclosed by Palicka. U.S. Patent No. 5,322,630 to Williams et al. discloses

amphoteric derivatives of a broad range of fatty polyamines, fatty amidoamines, fatty imidazoline amines and polyamines which are employed as oilfield corrosion inhibitors. There is, however, no disclosure or suggestion
5 in the Williams patent of the applications of the amphoteric derivatives of the polyamines herein disclosed, including neither the softening/texture modification of substrates such as paper, textiles, human skin surfaces and hair tresses, nor applications for metal working and
10 lubrication.

Furthermore, providing non-irritating softening agents for fabric or paper substrates, or to human skin or hair, has been a long felt need. Fabrics tend to become slightly harsher after wear and laundering. Moreover,
15 untreated personal hygiene facial tissue paper may be harsh and irritating to inflamed tissues, such as nasal orifice skin.

Various attempts have been made to soften fabrics such as suggested in patents directed to fabric softeners, for example, U.S. Patent No. 3,904,533 of Neiditch for a
20 liquid fabric softener, and U.S. Patent Nos. 4,237,155 of Kardouche and 5,376,287 of Borchert et al which describe antistatic fabric softener sheets, which include fabric-softening agents, such as cationic and nonionic
25 surfactants.

OBJECTS OF THE INVENTION

It is therefore an object of the present invention to define a family of amphoteric compounds comprising derivatives of aliphatic polyamines such as
30 diethylenetriamine wherein the polyamines are first converted to polyamides or imidazoline/amide derivatives thereof.

A further object of the present invention is to define and describe a process by which the above described
35 amphoteric derivatives of aliphatic polyamides [ADAPS] may be made.

It is another object of the present invention to provide an effective softener for various substrates which might contact human skin, as well as skin and hair substrates themselves.

5 It is a still further object of the present invention to provide amphoteric surface active agents for use in other applications, such as metal working, lubricating, etc.

10 SUMMARY OF THE INVENTION

The present invention relates to amphoteric derivatives of aliphatic polyamines [ADAPS] that have important industrial and personal care uses, such as, for example, softeners, lubricants, and conditioners, etc. The
15 ADAPS comprise derivatives of compositions which are intermediate aliphatic polyamides or imidazolines, and preferably aliphatic diamides, containing more than one substituent moiety selected from the group consisting of long alkyl chain fatty acids, esters and triglycerides,
20 such as derived from animal, vegetable or synthetic sources ranging in molecular distribution from butyric through erucic acids. (e.g. milkfat, soybean oil, rapeseed oil).

The intermediate amide compound is then converted into an amphoteric compound by reacting it with unsaturated
25 carboxylic acids, halogenated carboxylic acids, carboxylated epoxy compounds or in the case of the higher polyamines, acid anhydrides or polycarboxylic acids.

The carboxyalkylation step of the present invention attaches an alkyl carboxylic acid functional
30 group to at least one secondary internal amine nitrogen atom, thereby forming the amphoteric products of the present invention. The amphoteric product is thus a polyamide or imidazoline derivative of the aliphatic polyamine starting material.

35 Compounds containing acidic functional groups suitable for use in reacting with aliphatic polyamides in accordance with the present invention include alkyl

carboxyl groups [i.e., carboxylic acid functional moiety, COOH] where the carboxylic acid is derived from one or more unsaturated or halogenated carboxylic acids, carboxylated epoxy compounds, acid anhydrides and/or polycarboxylic acids with the proviso that the amphoteric composition must contain at least one ionizable nitrogen site. For the purposes of the present invention such above-mentioned unsaturated carboxylic acids, halogenated acids, carboxylated epoxy compounds, acid anhydrides or polycarboxylic acids, comprise an amphoteric forming group because the product produced by reacting with one of the acids is an amphoteric product.

DETAILED DESCRIPTION OF THE INVENTION

Consistent with the above discussion, a first specific group of ADAPs of the present invention may comprise amphoteric derivatives of diethylenetriamine [DETA] wherein the amphoteric derivatives of the present invention are prepared by first reacting DETA as a starting material with at least one member selected from long-alkyl-chain plant, animal or synthetic derived fatty acids, esters and triglycerides, such as, for example, compositions containing substituted or unsubstituted, branched or straight chain, saturated or unsaturated alkyl chain groups ranging in molecular distribution from butyric through erucic acids, that is, containing from 3 to 21 carbon atoms in addition to the carbonyl group.

An intermediate substituted DETA predominately diamide (preferably) is thus formed having fatty alkyl moieties of 3 to 21 carbon atoms.

Amphoteric forming agents suitable for use in reacting with aliphatic polyamides in accordance with the present invention include alkyl carboxyl groups (i.e., carboxylic acid functional moiety, COOH] where the carboxylic acid is derived from one or more unsaturated or halogenated carboxylic acids, or carboxylated epoxy compounds. Exemplary suitable amphoteric forming agents

include vernolic acid, acrylic acid, itaconic acid, chloroacetic acid, maleic anhydride, octadecenyl anhydrides and adipic acid.

5 A further group of products having novel applications is comprised of amphoteric imidazolines which are prepared according to the method hereinafter described for preparation of the DETA or other polyamines.

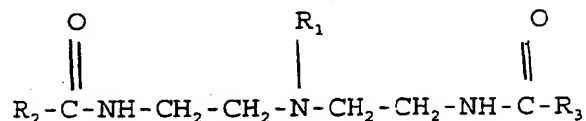
10 The following general structural formulas numbered 1 through 3 comprise the novel compounds of the present invention, and are further exemplified and represented in Tables 1 and 2 below.

Formula 1, below, generically shows diethylenetriamine [DETA] amphoteric derivatives more particularly set forth in Table 1 below. Formula 1 is a
15 diamide, having an amide group at each end of the molecule.

The central (secondary) nitrogen site on the molecule is acidified to form the amphoteric end product of the present invention.

FORMULA 1:

20



25

wherein:

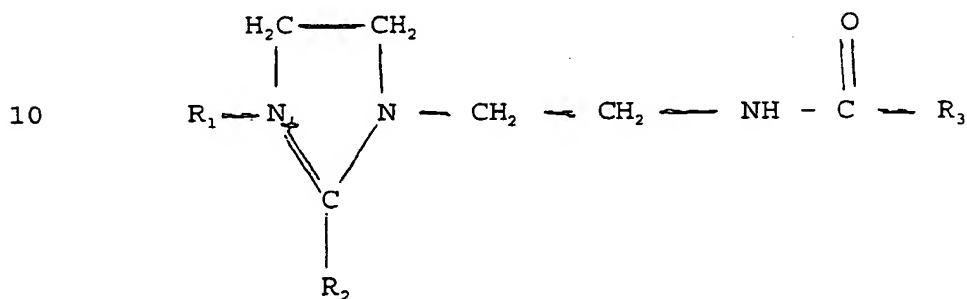
R₁ is a saturated or unsaturated aliphatic mono or poly carboxylic acid moiety having one or more carbonyl functional groups derived from intermediates containing olefinic, halogenated or epoxy reactive
30 sites, and may have one or more branched saturated or unsaturated, substituted or unsubstituted aliphatic chains containing from 2 to 18 carbon atoms; and

R₂ and R₃, which may be the same or different, can be a straight or branched, saturated or unsaturated,
35 substituted or unsubstituted alkyl chain of 3 to 21 carbon atoms.

Formula 2, below is a generic DETA-derived imidazoline, where the acidic functional group making the molecule amphoteric is attached to the quaternary nitrogen. Formula 2 is more particularly set forth in Table 1 below.

5

FORMULA 2:



wherein:

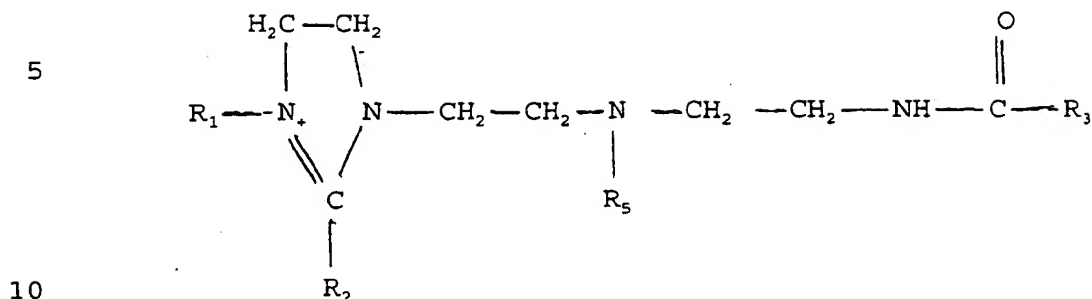
20 R_2 is a saturated or unsaturated aliphatic mono or poly carboxylic acid moiety having one or more carbonyl functional groups derived from intermediates containing olefinic, halogenated or epoxy reactive sites, and may have one or more straight or branched, saturated or unsaturated, substituted or unsubstituted aliphatic chains containing from 2 to 18 carbon atoms; and

25 R_2 and R_3 , which may be the same or different, can be a straight or branched, saturated or unsaturated, substituted or unsubstituted alkyl chain of 3 to 21 carbon atoms.

30 Formula 3, below, is similar to Formula 2, except that Formula 3 shows a generic triethylenetetramine [TETA] amidoimidazoline amphoteric. Formula 3 is more particularly set forth in Table 2 below. Except for the fact that Formula 3 is TETA derived rather than DETA derived, the discussion of Formula 2 above applies to Formula 3.

35

FORMULA 3:



wherein:

15 R₁ is a saturated or unsaturated aliphatic
mono or poly carboxylic acid moiety having one or
more carbonyl functional groups derived from
intermediates containing olefinic, halogenated or
epoxy reactive sites, and may have one or more
straight or branched, saturated or unsaturated,
substituted or unsubstituted aliphatic chains
20 containing from 2 to 18 carbon atoms;

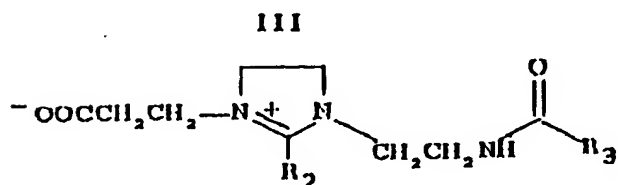
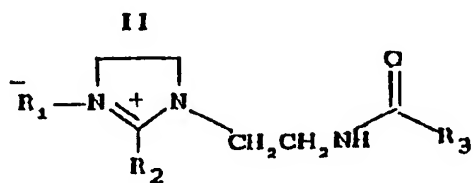
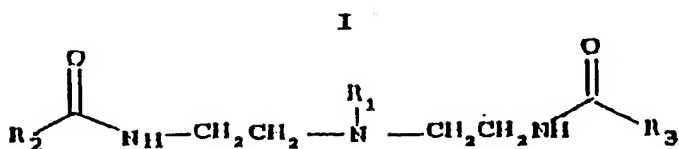
R₂ and R₃, which may be the same or different, can be straight or branched, saturated or unsaturated, substituted or unsubstituted alkyl chain of 3 to 21 carbon atoms; and

25 R₅ may be hydrogen, the same as R₁ or may be
a straight or branched, saturated or unsaturated,
substituted or unsubstituted alkyl chains having
3 to 21 carbon atoms derived from any appropriate
alkylating group including anhydrides.

30

35

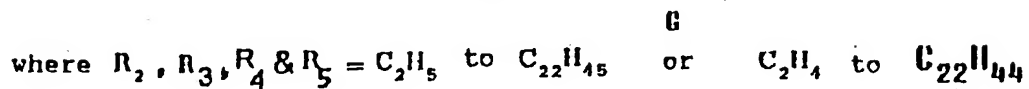
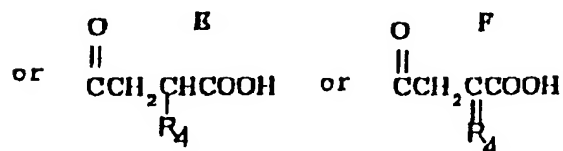
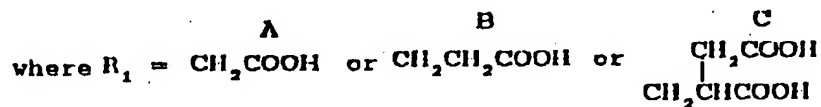
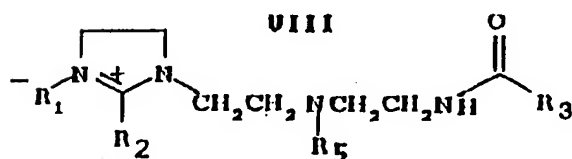
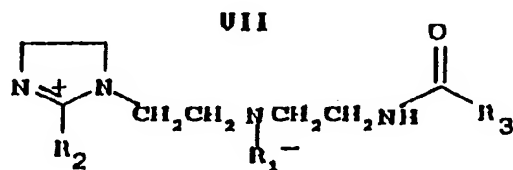
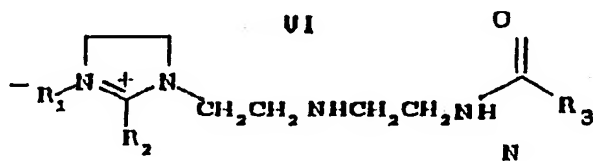
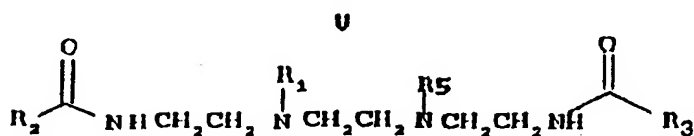
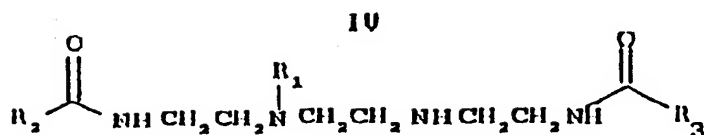
Table # 1
Polyamine-Derived Amphoteric
DETA Derivatives



where $\text{R}_1 = \overset{\text{A}}{\text{CH}_2\text{COOH}}$ or $\overset{\text{B}}{\text{CH}_2\text{CH}_2\text{COOH}}$ or $\overset{\text{C}}{\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{CH}_2\text{CHCOOH} \end{array}}$

where R_2 & $\text{R}_3 = \overset{\text{G}}{\text{C}_2\text{H}_5}$ to $\text{C}_{22}\text{H}_{45}$ or $\overset{\text{H}}{\text{C}_2\text{H}_4}$ to $\text{C}_{16}\text{H}_{36}$

Table # 2
Polyamine-Derived Amphoteric
TETA Derivatives



The DETA polyamide and imidazoline-amide DETA and TETA intermediate compositions suitable for use in the preparation of amphoteric compositions of the present invention in accordance with the practice of the invention are well known and include those derived from substituted or unsubstituted, branched or straight chain, saturated or unsaturated fatty acids, esters, or triglycerides with fatty alkyl amide moieties containing from 4 to 22 carbon atoms. Examples of suitable fatty acids, esters or triglycerides include octanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, methyl esters or glyceride esters of such acids or mixtures thereof as are found in coconut oil, palm oil, sunflower oil, soybean oil, rapeseed oil, castor oil, fish oil, tallow fat, milk fat, lard and other natural sources or may be of synthetic origin.

The materials of the present invention are embodied in reactions carried out under the following conditions, as noted in the Examples below.

For example, amphoterics are derived from DETA-diamides, such as shown in Example 1 below, wherein linoleic-DETA diamide monopropionate is produced, from a reaction wherein soybean oil and diethylenetriamine are first mixed. In a second reaction, acrylic acid is added.

In Example 2 below, oleic DETA diamide is produced from a mixture of olive oil and diethylenetriamine.

In Example 3 below, to the amide of example 2 there is added acrylic acid, to produce oleic DETA diamide monopropionate, or, as noted in Example 4 below, there is added itaconic acid, to produce oleic DETA diamide mono-3-carboxybutyrate.

As noted in Example 5 below, caprylic-capric-DETA diamide propionate is produced from the reaction of a mixture of caprylic-capric triglyceride and

diethylenetriamine, which is further reacted with acrylic acid.

Furthermore, as noted in Example 6 below, dioleoyl-imidazoline-amide-propionate is produced from two reactions, namely a reaction of a mixture of oleic acid and diethylenetriamine, which is further reacted with glacial acrylic acid.

The foregoing present invention includes aliphatic intermediate derivatives of polyamine compounds resulting in amphoteric imidazolines, polyamides, and preferably diamides having a carboxyalkylated secondary, internal amine nitrogen site. Carboxyalkylation is achieved by reacting a substituted polyamine or polyamide intermediate with an amphoteric-forming group consisting of halogenated carboxylic acids, unsaturated carboxylic acids, suitable epoxy compounds, or anhydrides in the case of higher polyamines such as TETA.

The resulting compounds are useful as softeners for tissues, fabrics, hair and skin, and a novel method of softening is disclosed based on the use of the compounds described herein. Because the novel compounds of the present invention provide antiwear properties, a method of using these compounds of the present invention in metal working is also taught.

It is therefore a further aspect of the invention to use the amphoteric derivative compositions of the invention, for example, as softening agents for facial tissue paper, textiles, hair and human skin in amounts of 0.1 to 10% by weight and for metal working applications such as lubricating and antiwear compositions in amounts of from about 0.1% by weight.

The invention is noted in the following illustrative examples, which are provided herein for the purposes of illustration only, and are not intended to limit the scope of the present invention, as noted in the appended claims.

Pertinent examples of preparation of the novel materials of the present invention are embodied in reactions carried out under the following conditions.

5

Example 1.

Linoleic-DETA Diamide Monopropionate

To a three-necked flask fitted with a stirrer, thermometer and reflux condenser is charged 584.0gms. soybean oil and 103.0gms. [DETA] diethylenetriamine. The reaction mixture is heated at 180-190°C for four hours, at which time the alkali value drops to 90 (mm KOH/g). After cooling to 70°C, 79.2gms. acrylic acid was added. The addition is exothermic and the temperature rises to 102°C. The temperature is maintained at 90-100°C for an additional four hours. After the reaction is complete, the final alkali value is 75, the acid value is 64 and the 10% pH in isopropyl alcohol/water is 4.8.

20

Example 2.

Oleic-DETA-Diamide

To a three-necked flask fitted with a stirrer, thermometer and reflux condenser is charged 584.0 gms olive oil and 103.0 gms diethylenetriamine [DETA]. The reaction mixture is heated at 180-190°C for four hours at which time the alkali value drops to 90 (mm KOH/g).

25

Example 3.

Oleic-DETA Diamide-Monopropionate

To 68.7gms of the amide of above Example 2 at 90°C, in a reaction vessel is charged 7.9gms of acrylic acid. The mixture is heated with agitation at 95-105°C for five hours until reaction is complete, as evidenced by disappearance of acrylic acid.

35

Example 4.

Oleic-DETA Diamide Mono-3-Carboxybutyrate

To 68.7 gms of the amide of Example 2 at 90°C is charged 14.3gms of solid itaconic acid. The mixture is heated with agitation at 95-105°C for 5 hours, until reaction is complete, as evidenced by disappearance of itaconic acid.

Example 5.

Caprylic-Capric-DETA Diamide Propionate

To a three-necked flask fitted with a stirrer, thermometer and reflux condenser there is charged 330gms of a caprylic capric-triglyceride, of the trade name Neobee M5, from Stepan Chemical Co., and 103gms of diethylenetriamine. The mixture is heated at 180-185°C for four hours, after which the alkali value dropped to 135 (mm KOH/g). After cooling to 70°C, 72gms of acrylic acid are added and the mixture heated at 90-100°C for four hours, until the reaction is complete, as evidenced by disappearance of acrylic acid.

Example 6.

Diioleoyl-Imidazoline-Amide-Propionate

To a three-necked flask fitted with a stirrer, thermometer and distillation condenser there is charged 564gms. of oleic acid and 103.2 gms of diethylenetriamine. The reaction mixture is heated to 155°C where water of reaction begins to distill. The temperature is allowed to rise gradually to 190-200°C over about three hours at which time the alkali value is 105.6 and the acid value is 4.10. Vacuum was then applied gradually until a pressure of 11 mm Hg is reached. Samples are taken periodically and checked for imidazoline content. After about three hours at 190°C and 11 mm Hg, an imidazoline content of 90% is obtained. The product is then cooled to 70°C and the vacuum is released. 72 gms of glacial acrylic acid is added. The exothermic reaction carried the temperature to 95°C, which

is maintained for an additional 4 hours, until reaction is complete.

5

Example 7.

Milk Lipids - DETA Diamide Monopropionate

To a three-necked flask fitted with a stirrer, thermometer and reflux condenser is charged 490 gms. milk lipids and 103.0 gms. of diethylenetriamine (DETA). The reaction mixture is heated at 180-190°C for four hours, at which time the alkali value drops to 93 (mm KOH/g). After cooling to 70°, 72 gms of acrylic acid is added. The addition is exothermic and the temperature rises to 102°C. The temperature is maintained at 90-100°C for an additional four hours. After the reaction is complete, the final alkali value is 88, the acid value is 76 and the 10% pH in isopropyl alcohol/water is 65.

20

Example 8.

Milk Lipids-Imidazoline-Amide Dipropionate

To a three-necked flask fitted with a stirrer, thermometer and reflux condenser is charged 490gms of milk lipids and 103gms of diethylenetriamine (DETA). The reaction mixture is heated at 155°C where water of reaction begins to distill. The temperature is allowed to rise gradually to 190-200°C over about three hours, at which time the alkali value is 96 (mm KOH/g).

Vacuum is then applied gradually until a pressure of 11mm of Hg is reached. Samples are taken periodically and checked for imidazoline content. After about three hours at 190°C and 11mm Hg, an imidazoline content of 90% is obtained. The product is cooled to 70°C and the vacuum is released.

To the molten imidazoline is added 172gms of methylacrylate and the mixture is heated at 90 to 100°C for four hours. After which the methylacrylate content is less than 5%. The reaction mixture is charged to a separate

flask containing a solution of 120gms of 50% caustic soda, 522gms of propylene glycol and 729gms of water and heated at 90° to 95°C for two hours to hydrolyze the methyl ester.

After cooling to 50°C, the reaction product is a clear
5 amber liquid with total solids of 34.6% having a 10% pH in isopropyl alcohol/water of 10.1.

Example 9.

Table #3 below outlines the procedure used, as well as the results obtained in evaluating several
10 diethylenetriamine (DETA) amphoteric derivatives (Samples A-1, A-2, A-3 and A-4) for their softening properties on tissue paper.

The results of Table #3 indicate that all of the DETA-derived amphoterics tested (Samples A-1, A-2, A-3 and
15 A-4) exhibited very good paper softening properties and are superior to the Control Sample 1, namely, a DETA imidazolinium quaternary derivative tested.

The amphoteric derivatives, Samples A-1, A-2, A-3 and A-4 in Table #3, are found to be very effective in
20 softening challis wool swatches which are soaked in aqueous dispersions of the amphoterics and then rinsed and allowed to dry using the procedure similar to that used with facial tissue paper. It is also noted that the amphoteric derivative samples are effective in depositing a residual,
25 smooth conditioned feeling to human skin and hair.

TABLE #3

FACIAL TISSUE SOFTNESS EVALUATIONS OF DIETHYLENETRIAMINE
(DETA)

DERIVATIVES

30

Procedure:

1. 1% active test solutions/dispersions are prepared in deionized water and adjusted with lactic acid to the 4-8 pH range.
- 35 2. Evaluations are conducted using 8" x 9" untreated paper tissues weighing approximately 1.5 grams each. The lower half of each tissue is dipped briefly into the 1%

active solution being tested, then the tissues are withdrawn, allowed to drain, dried and equilibrated for several hours at ambient temperature and humidity. A deionized water blank is included in the test regimen.

- 5 3. Treated tissues are evaluated (undipped versus dipped portions) and ranked for softness by a small R&D expert panel. Numerical softness rankings are assigned as follows:

- 10 0 = Poor/harsh texture
 1 = Fair
 2 = Good
 3 = Very Good
 4 = Excellent/very soft texture

After Dipping in 1% Active Dispersions

- 15 Followed by Draining and Drying

1% Active in Water Material Tested

Softness/Texture

Sample A-1	Milkfat DETA Imidazolinium Amphomonopropionate	3.5
Sample A-2	Soybean Oil DETA Diamide Amphomonopropionate	3.5
20 Sample A-3	Rapeseed Oil DETA Diamide Amphomonopropionate	3
Sample A-4	Milkfat DETA Imidazolinium Amphomonopropionate	3/3.5
Control 1	Milkfat DETA Imidazolinium Quaternary	2.5
Control 2	Deionized Water Blank	0

- 25 All of the DETA amphoteric derivatives tested exhibit very good paper softening properties and are superior to the quaternary softener (Control 1).

Example 10.

- 30 Table #4 below shows a comparison of two DETA-derived amphoterics, Sample B-1, namely, a disoya DETA amphomonopropionate as prepared in Example 1 and Sample B-2, namely, a di-caprylic-capric DETA amphomonopropionate as prepared in Example 5 versus a Control, namely, a
35 commercial milk lipid amido propyl betaine, when used in a bath and shower cleanser. The DETA derivatives of Samples B-1 and B-2 exhibits better conditioning on skin and hair,

and better foam in the case of the caprylic-capric amphoteric than the Control, namely, milk lipid amidopropyl betaine.

5

TABLE #4

Bath and Shower Cleansers

Soya & C8-10 DETA Diamide Amphoterics

vs.

Milk Lipid Amidopropyl Betaine

10	<u>Raw Material</u>	<u>R67.00-11A % by Weight</u>	<u>R67.00-11B % by Weight</u>	<u>R70.01-127 % by Weight</u>
----	---------------------	-----------------------------------	-----------------------------------	-----------------------------------

	Deionized Water	45	45	45
--	-----------------	----	----	----

	Sodium Chloride	1	1	1
--	-----------------	---	---	---

15	Sodium Lauryl Sulfate (28%)	10	10	10
----	-----------------------------	----	----	----

	MONALAC MPL	2	2	2
--	-------------	---	---	---

	MONALAC MO	2	2	2
--	------------	---	---	---

20	Sodium Laureth Sulfate (26%)	35	35	35
----	------------------------------	----	----	----

	Milk Lipid Amidopropyl Betaine			
--	--------------------------------	--	--	--

	(MONALAC MAB) Control	5	-	-
--	-----------------------	---	---	---

	Sample B-1 (Example 1)	-	5	-
--	------------------------	---	---	---

25	Sample B-2 (Example 5)	-	-	5
----	------------------------	---	---	---

The ingredients are added in the order listed. The pH is adjusted to 6.0-6.5 and desired preservatives, fragrances, etc. are added.

30	Appearance:	Clear Liquid	Clear yellow Liquid	Opaque, Light Yellow Liquid
----	-------------	--------------	---------------------	-----------------------------

	Viscosity (ambient temp.)	2,000 cps	1,500 cps	1000
--	---------------------------	-----------	-----------	------

35	Viscosity with an additional 0.25% NaCl:	6,500 cps	3,500 cps	800
----	--	-----------	-----------	-----

	pH:	6.37	6.38	6.36
--	-----	------	------	------

40 After washing, all of the products give a very smooth conditioned feel to the skin and hair, but the di-

soya and di(C8-10) amphoteric, Sample B-1 and B-2, exhibit a higher level of smoothness than the milk lipid amidopropyl betaine. In addition, the di(C8-10) amphoteric (Sample B-2) exhibits much higher foam levels during washing.

Further application testing is carried out on polyamine amphoteric derivatives of the present invention in the areas of lubrication, hydraulic fluids, metalworking and anti-wear additives.

Example 11.

Table #5 below shows a list of Samples C-1 through C-8 tested for metal working, lubrication and anti-wear additives. The "structure type" refers to the chemical structure noted in Tables 1 and 2 herein, wherein the Roman numerals refer to the basic molecular structure and the Alphabetical designations refer to the specific designations for the various "R" groups in the formulas of Tables 1 and 2. Performance data are shown for experimental compositions evaluated in the zwitterionic acid forms, as well as the long chain alkylamine salts.

TABLE #5

DESCRIPTIONS OF SAMPLES TESTED

For Metalworking & Hydraulic Fluid Additives

Sample Designation	Structure Type	R_2 & R_3	Acid Form or Neutralizing Agent
C-1	I-A	$C_{17} H_{34}$	Acid Form
C-2	III	$C_{17} H_{34}$	Tridecyloxypropylamine
C-3	III	$C_{17} H_{34}$	Acid Form
C-4	I-C	$C_{17} H_{34}$	Acid Form
C-5	I-C	$C_{17} H_{34}$	Tridecyloxypropylamine
C-6	I-B	$C_{17} H_{34}$	Tridecyloxypropylamine
C-7	I-C	$C_{17} H_{34}$	Tridecyloxypropylamine
C-8	I-B	Soya	Acid Form

Table #6 below shows that in ASTM 2783 studies of blends with paraffinic and naphthenic derived mineral oils,

marked decreases in coefficients of friction and steel ball scar diameters are noted for several of these derivatives.

TABLE #6

5 Results of Four-Ball Method Testing (ASTM D2783)

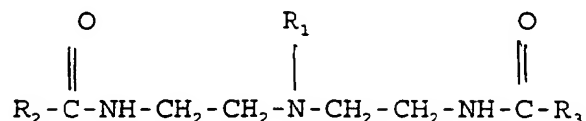
<u>Sample Tested</u> <u>@ 0.1% in</u> <u>Mineral Oil</u>	<u>Coefficient</u> <u>of Friction</u>	<u>Scar</u> <u>Diameter</u> <u>(mm.)</u>	<u>2% ZnDTP</u> <u>Added to 0.1%</u> <u>in Mineral Oil</u>	<u>Coefficient</u> <u>of Friction</u>	<u>Scar</u> <u>Diam</u> <u>(mm.)</u>
C-6	0.0493	0.9	C-6	0.0586	0.5
C-7	0.0595	0.9	C-7	0.0510	0.4
C-2	0.0595	0.9	C-2	0.0782	0.5
C-1	0.0833	0.7	C-1	0.0510	0.5
C-5	0.0935	0.8	C-5	0.0773	0.5
Monacor 39*	0.0799	0.5	Monacor* 39	0.0595	0.5
			ZnDTP alone	0.0952	0.6

* Commercial
test products

** Zinc dialky
dithio
phosphate

CLAIMS:

1. Texture and softening compositions for a wide range of paper, textile and human substrates comprising amphoteric compositions that are represented by the formula:



wherein:

R_1 is a saturated or unsaturated aliphatic mono or poly carboxylic acid moiety having one or more carboxyl functional groups derived from intermediates containing olefinic, halogenated or carboxylated epoxy reactive sites, and having one or more straight or branched, saturated or unsaturated aliphatic chains containing from 2 to 18 carbon atoms; and

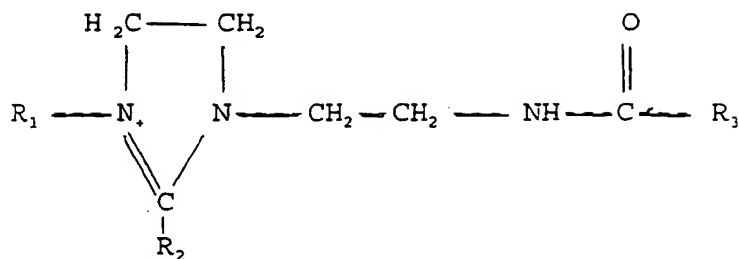
R_2 and R_3 , which may be the same or different, are a straight or branched, saturated or unsaturated alkyl chains of 3 to 21 carbon atoms.

2. Texture and softening compositions as in Claim 1, wherein further R_1 is derived from a chlorinated carboxylic acid having from 2 to 6 carbon atoms.

3. Texture and softening compositions as in Claim 1, wherein further R_1 is derived from a carboxylic acid having an unsaturated alkyl carbon chain.

4. Texture and softening compositions as in Claim 1, wherein further R_1 is a carboxylic acid functional group having an unsaturated alkyl carbon chain.

5. Texture and softening compositions for a wide range of paper, textile and human substrates comprising amphoteric compositions represented by the general formula:

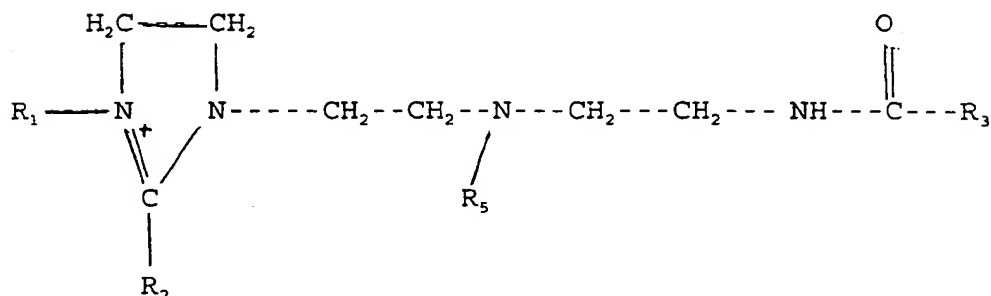


wherein:

R_1 is a saturated or unsaturated aliphatic, mono or poly carboxylic acid moiety having one or more carboxyl functional groups derived from intermediates containing olefinic, halogenated epoxy or anhydride reactive sites, and having one or more straight or branched, saturated or unsaturated aliphatic chains containing from 2 to 18 carbon atoms; and

R_2 and R_3 , which may be the same or different, is a straight or branched, saturated or unsaturated alkyl chain of 3 to 21 carbon atoms; or

Compositions represented by the formula:



wherein:

R_1 is a saturated or unsaturated aliphatic mono or poly carboxylic acid moiety having one or more carboxyl functional groups derived from intermediates containing olefinic, halogenated, epoxy or anhydride reactive sites, and having one or more straight or branched saturated or

unsaturated aliphatic chains containing from 2 to 18 carbon atoms;

R_2 and R_3 , which may be the same or different, is a straight or branched, saturated or unsaturated alkyl chain of 3 to 21 carbon atoms, and

R_5 which is hydrogen, the same as R_1 , or is derived from an alkylating group.

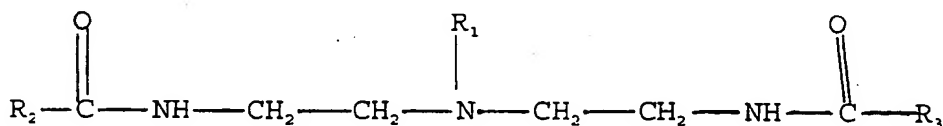
6. Texture and softening compositions as in Claim 5, wherein further, R_1 is an aliphatic mono or poly carboxylic acid moiety having one or more carboxyl functional groups, and wherein further, R_2 and R_3 are a straight or branched chain, saturated or unsaturated aliphatic chains having from 3 to 21 carbon atoms.

7. Texture and softening compositions as in Claim 5, wherein further, R_1 is derived from a chlorinated carboxylic acid functional group having from 2 to 6 carbon atoms.

8. Texture and softening compositions as in Claim 5, wherein further, R_1 is a carboxylic acid functional group having an unsaturated alkyl carbon chain.

9. Texture and softening compositions as in Claim 5, wherein further, R_1 is a chlorinated carboxylic acid functional group having an unsaturated alkyl carbon chain.

10. Texture and softening compositions as in claim 1 represented by the general Formula as set forth below:



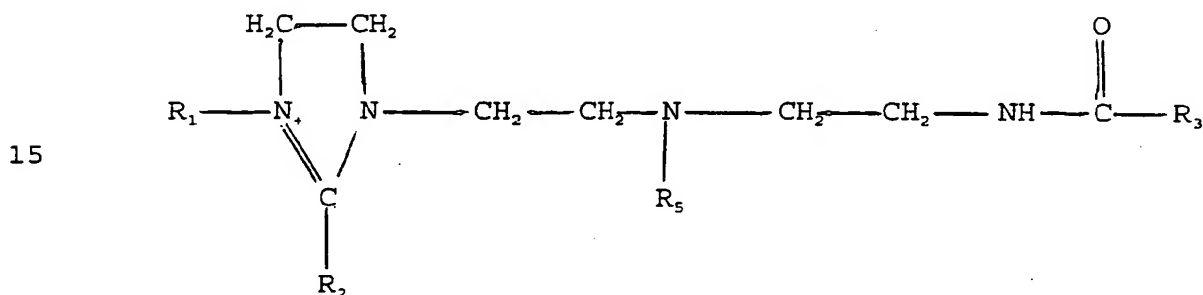
wherein:

R_1 is a saturated or unsaturated aliphatic, mono or poly carboxylic acid moiety having one or more carboxyl functional groups derived from

intermediates containing olefinic or epoxylated epoxy reactive sites, having one or more straight or branched, saturated or unsaturated aliphatic chains containing from 2 to 18 carbon atoms; and

5 R_2 and R_3 , which may be the same or different, are straight or branched, saturated or unsaturated alkyl chain of 3 to 21 carbon atoms.

11. Texture and softening compositions as in Claim 5 of the general Formula 3 as represented by the
10 following:



20 wherein:

R_1 is a saturated or unsaturated aliphatic mono or poly carboxylic acid moiety having one or more carboxyl functional groups derived from intermediates containing olefinic, halogenated, epoxy or anhydride reactive sites, and having one
25 or more straight branched saturated or unsaturated aliphatic chains containing from 2 to 18 carbon atoms;

R_2 and R_3 , which may be the same or different, is a straight or branched, saturated or unsaturated alkyl chain of 3 to 21 carbon atom; and

R_5 which is hydrogen, the same as R_1 , or is derived from an alkylating group.

35 12. Texture and softening compositions as in Claim 11, wherein further R_1 is a chlorinated carboxylic acid functional group having from 2 to 6 carbon atoms.

13. Texture and softening compositions as in Claim 11, wherein further R_1 is a carboxylic acid functional group having an unsaturated alkyl carbon chain.

5 14. A method of softening paper, textile and human substrates comprising contacting the substrate of an object to be softened with compositions comprising an effective amount of the compositions of claim 1; and, permitting the object to dry.

10 15. The method of claim 14 wherein the substrate to be softened is paper.

16. The method of claim 14 wherein the substrate to be softened is textile fabric.

15 17. A method of softening paper, textile and human substrates comprising contacting the substrate of an object to be softened with compositions comprising an effective amount of the compositions of claim 5; and permitting the object to dry.

18. Metal treating compositions comprising an effective amount of the composition of claim 1.

20 19. Metal treating compositions comprising an effective amount of the composition of claim 5.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99-18974

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C11D 1/58, 1/62, 1/66

US CL : 510/500, 501, 504

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/500, 501, 504

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN structure search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHI, M., QU, R. Synthesis and Bactericidal Activity of Fatty Acyl Ethylene Glycine and Its Cyclocondensation Products (Abstract). April 1974. Pages 184-187.	1-4, 10, 11, 14-17, 19
A	US 4,362,737 A (SCHAFER et al) 07 December 1982, see entire text.	5-9, 12, 13, 18 and 19

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z

document member of the same patent family

Date of the actual completion of the international search

13 DECEMBER 1999

Date of mailing of the international search report

27 JAN 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
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INTERNATIONAL SEARCH REPORT

International application No.
PCT-US99/18974

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT:US99-18974

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-4, 10, 11, 14-17 AND 19, drawn to compositions containing bis-amideamines.

Group II, claim(s) 5-9, 12, 13, 18 and 20, drawn to compositions containing imidazolyl compounds.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: Any structural feature which unites the two inventions does not make a contribution over the prior art, as shown by reference marked to Shi et al., Riyong Huaxue Gongye, 1992, 4, 184-187.